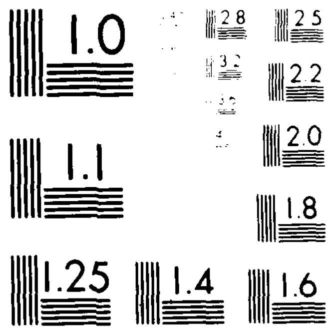
AD-A186 044 DC CONDUCTIVITY STUDIES OF AN HYDROXIDE ION CONDUCTOR 1/1
AT INTERMEDIATE TEM (U) STANFORD UNIV CA DEPT OF
MATERIALS SCIENCE AND ENGINEERING

UNCLASSIFIED S CROUCH-BAKER ET AL 30 JUL 87 TR-7 F/G 7/4 NL


1.0
2.8
2.5
2.2
2.0
1.1
1.8
1.25
1.4
1.6

REPORT DOCUMENTATION PAGE

AD-A186 044

DTIC ELECTE SEP 30 1987 S D

REPORT SECURITY CLASSIFICATION UNCLASSIFIED	1b. RESTRICTIVE MARKINGS
SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited
DECLASSIFICATION/DOWNGRADING SCHEDULE	
PERFORMING ORGANIZATION REPORT NUMBER(S) # 7	5. MONITORING ORGANIZATION REPORT NUMBER(S) N00014-84-K-0648
NAME OF PERFORMING ORGANIZATION R.A. Huggins Stanford University — 6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research Dr. Harold Guard
ADDRESS (City, State and ZIP Code) Dept. Mat. Sci. & Eng. Peterson 550I Stanford, CA 94305-2205	7b. ADDRESS (City, State and ZIP Code) Chemistry Division, Code 413 800 North Quincy Street Arlington, VA 22217
NAME OF FUNDING/SPONSORING ORGANIZATION — 8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
ADDRESS (City, State and ZIP Code)	10. SOURCE OF FUNDING NOS. PROGRAM ELEMENT NO. / PROJECT NO. / TASK NO. 634-845 / WORK UNIT NO.

TITLE (Include Security Classification)
"DC Conductivity Studies of an Hydroxide Ion Conductor at Intermediate Temperatures"

PERSONAL AUTHOR(S)
S. Crouch-Baker and R.A. Huggins

TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Yr., Mo., Day)	15. PAGE COUNT
Technical	FROM ______ TO ______		

SUPPLEMENTARY NOTATION
Submitted as an Accelerated Brief Communication to the Journal of the Electrochemical Soc

COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB. GR.	

ABSTRACT (Continue on reverse if necessary and identify by block number)

In this study, preliminary experiments are conducted on an hydroxide ion-conducting electrolyte, which may have potential for application to the electrolysis of steam at intermediate temperatures. In this work, the DC conductivity of wet Li_5AlO_4 samples has been measured as a function of temperature and applied voltage. It is proposed that, under the conditions employed in this work, DC charge conduction is due to the transport of hydroxide ions derived from the LiOH contained in the structure, rather than by electronic species.

DISTRIBUTION/AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS ☐	21. ABSTRACT SECURITY CLASSIFICATION
NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE NUMBER (Include Area Code) — 22c. OFFICE SYMBOL

FORM 1473, 83 APR — EDITION OF 1 JAN 73 IS OBSOLETE.

ms. 894
cf. ms. 851

87 9 23 026

OFFICE OF NAVAL RESEARCH

Contract No. N00014-84-K-0648

Task No. 634-845

Technical Report No. 7

DC Conductivity Studies of an Hydroxide Ion Conductor at Intermediate Temperatures

by

S. Crouch-Baker and R. A. Huggins

Submitted to the Journal of the Electrochemical Society

Stanford University
Department of Materials Science and Engineering
Stanford, CA 94305-2205

July 30, 1987

DC Conductivity Studies of an Hydroxide Ion Conductor at Intermediate Temperatures

S. Crouch-Baker* and R. A. Huggins*

Department of Materials Science and Engineering

Stanford University, Stanford CA 94305

INTRODUCTION

There is continued interest in the development of an electrochemical process for the production of hydrogen. Much of the current activity in this area involves the development of high temperature steam electrolysis technology operating at about 1000°C, which shows promise for significant reductions in electrical energy requirements compared to traditional water electrolysis at ambient, or near ambient, temperatures. This is due to favorable thermodynamic and kinetic factors at elevated temperatures (1,2). Other commercial approaches have involved the use of systems containing solid ion-exchange polymer electrolytes at 80°C (3). In addition, several proton - conducting solid electrolytes have been investigated that might be useful for this purpose. It has been found, however, that those with the highest conductivity, based upon the transport of protons among donor/acceptor arrays, such as the layered hydrate $HUO_2PO_4 \cdot 4H_2O$ (HUP) and the beta" aluminas containing H_3O^+ and/or NH_4^+, ions decompose at about 50°C and 200°C, respectively (4,5).There has also been some work on the use of proton conductors based upon doped $SrCeO_3$ in the temperature range 700 - 900°C (6,7). But in this case there is appreciable electronic conductivity at higher temperatures, and the electrolyte resistance is quite high.

On the other hand, it has been pointed out that there would be considerable thermodynamic, as well as practical, advantages if suitable materials could be found that would permit the electrolysis of steam at intermediate temperatures (8). This communication describes the results of some preliminary experiments on an hydroxide ion-conducting electrolyte which may have potential for application in this area.

The ionic conductivity and thermal behaviour of Li_5AlO_4 have previously been studied in both wet and dry environments (9-11). The results of AC conductivity experiments, using silver electrodes, indicated a large increase in the ionic conductivity of Li_5AlO_4 in a wet environment in the temperature range 415 - 450°C. This was not observed in a dry environment. A similar increase was also found with pure LiOH, and it was suggested (10,11) that the large conductivity increase in Li_5AlO_4 in a wet environment is due to the formation of LiOH in the grain boundaries, according to the reaction:

$$Li_5AlO_4 + 2\,H_2O = 4\,LiOH + LiAlO_2$$

In addition, the results of DC polarization experiments were interpreted (9-11) as indicating the presence of appreciable amounts of electronic conduction in some cases.

In this work, the DC conductivity of wet Li_5AlO_4 samples has been measured as a function of temperature and applied voltage. It is proposed that, under the conditions employed in this work, DC charge conduction is due to the transport of hydroxide ions derived from the LiOH contained in the structure, rather than by electronic species.

EXPERIMENTAL METHODS

Li_5AlO_4 was prepared by heating together reagent grade Li_2O and Al_2O_3 in air at 600°C, as described previously (9-11). Disk-shaped samples were prepared by cold-pressing, and they were sintered in air at 600°C prior to use. DC conductivity measurements were made using Pt foil electrodes pressed against the samples, which were held in a glass tube lined with Al foil. At higher voltages, steady values were obtained after only a few minutes. Measurements were carried out in a flowing Ar atmosphere saturated with water.

RESULTS AND DISCUSSION

Fig. 1 shows representative data obtained for the variation of conductivity with reciprocal temperature in the temperature range 390 - 540°C. These data are similar to those obtained previously (9-11), with the conductivity rising sharply in the range 415 - 450°C. It also has been found to rise less steeply above that temperature. However, as shown in that figure, the conductivity depends upon the applied voltage. This relationship is illustrated in Fig. 2 at two different temperatures. It is apparent

*Electrochemical Society Active Member.

Key words: conductivity, hydroxide, electrolysis.

that, in this range, the conductivity rises sharply at approximately 1 V and begins to level off at higher voltages. In carrying out these experiments, continuous DC conductance, i.e. without current interruption, was observed for up to ten hours. The results were considerably different when measurements were made in a water-free environment. The initial conductance was lower, and decreased rapidly to negligible values.

The sharp rise in apparent conductivity shown in Fig. 2 is due to a change in the electrode reactions at approximately 1 V. This value corresponds closely to that calculated for the electrolysis of water vapor (1.07 V at 500°C) in the relatively narrow temperature range studied here. Hence, above 1 V the electrode reactions produce and consume OH^- ions, and are presumed to be:

$$\text{Negative}: 2\,H_2O(g) + 2\,e^- = 2\,OH^- + H_2(g)$$

$$\text{Positive}: 2\,OH^- = H_2O(g) + 1/2\,O_2(g) + 2\,e^-$$

Thus the overall reaction results in the transport of OH^- through the electrolyte, presumably with the decomposition of water vapor, leading to the production of hydrogen on the negative electrode side and oxygen on the positive electrode side of the cell.

Hence, such materials show promise as potential electrolytes for the electrolysis of steam at intermediate temperatures. Further studies are underway.

ACKNOWLEDGEMENT

This work was supported, in part, by the Office of Naval Research.

REFERENCES

1. F. J. Salzano, G. Skaperdas, and A. Mezzina, "Hydrogen Energy Progress V", Vol 2, p. 787, ed. by T.N. Veziroglu and J.B. Taylor, Pergamon Press (1984).
2. W. Doenitz, G. Dietrich, E. Erdle, and R. Streicher, "Hydrogen Energy Progress VI", Vol 1, p. 271, ed. by T. N. Veziroglu, N. Getoff, and P. Weinzierl, Pergamon Press (1986).
3. R. Oberlin and M. Fischer, "Hydrogen Energy Progress VI", Vol 1, p. 333, ed. by T. N. Veziroglu, N. Getoff, and P. Weinzierl, Pergamon Press (1986).
4. J. S. Lundsgaard, J. Malling, and S. Yde-Andersen, "Solid State Protonic Conductors II", p. 400, ed. by J. B. Goodenough, J. Jensen and M. Kleitz, Odense Univ. Press (1983).
5. J. O. Thomas, A. Eriksson, J. Kjems, and A. Petford, "Solid State Ionics - 85", p. 612, ed. by J. B. Boyce, L. C. DeJonghe and R. A. Huggins, North-Holland (1985).
6. H. Iwahara, T. Esaka, H. Uchida, and N. Maeda, Solid State Ionics, 3/4, 359 (1981).
7. H. Iwahara, H. Uchida, and I. Tamasaki, J. Hydrogen Energy, 12, 73 (1987).
8. F. J. Salzano, "Hydrogen Energy Progress VI", Vol 1, p. 377, ed. by T.N. Veziroglu, N. Getoff, and P. Weinzierl, Pergamon Press (1986).
9. I. D. Raistrick, C. Ho, and R. A. Huggins, Mat. Res. Bull., 11, 953 (1976).
10. R. T. Johnson, Jr., R. M. Biefeld, and J. D. Keck, Mat. Res. Bull., 12, 577 (1977).
11. R. M. Biefeld and R. T. Johnson, Jr., J. Electrochem. Soc., 126, 1 (1979).

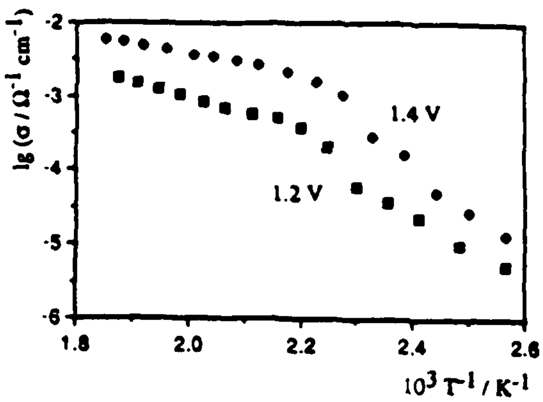


Fig. 1. Variation of DC conductivity with reciprocal temperature for wet Li_5AlO_4. Results are shown for two different applied voltages.

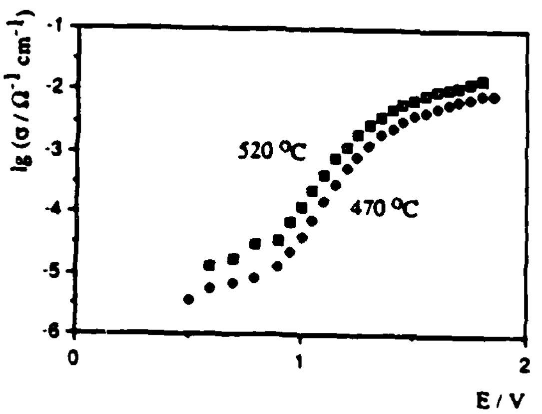


Fig. 2. Variation of DC conductivity with applied voltage, E, for wet Li_5AlO_4. Results are shown for two different temperatures.

END
DATE
FILMED
DEC.
1987